Task ID: 425.022
Task Title: Environmentally-Friendly Cleaning of New Materials and Structures for Future Micro- and Nano-Electronics Manufacturing
Deliverable: Report on the preliminary selection of cleaning methods for Ge and Si-Ge surfaces

Summary Abstract:

The purpose of the proposed project is to develop new environmentally-friendly cleaning recipes and procedures for cleaning of two types of surfaces and materials (low k dielectrics and Ge, Si-Ge surfaces). These represent both front-end and back-end materials and processes that have significant cleaning issues and major environmental impact due to their unique physical and chemical properties which are very dissimilar to the conventional materials.

Technical Results and Data:

Subtask 1. Cleaning of Low-k Dieletrics: The removal of etch residues deposited on the sidewalls of low-k materials requires chemistries which are "gentle" and benign to these materials. The chemical formulations should be able to remove the residues without swelling or chemically reacting with the low-k materials. Additionally, the formulations should be able to penetrate the high aspect ratio features, wet areas of different composition and be removable by water rinsing. Efficient wetting and penetration of hydrophobic areas requires low surface tension fluids. Hence, use of aqueous chemistries for hydrophobic materials need suitable additives to reduce the surface tension of water. These additives must not alter the dielectric properties of the low-k materials. An additional challenge is drying the structures after cleaning, without leaving residues and water spots.

In the case of porous dielectrics, penetration and transport of cleaning fluids into and out of the fine pores is a complex process. Understanding the dynamics of these processes and the bottleneck in the overall cleaning process is key in lowering the chemical and energy usage, and developing environmentally friendly chemistries and methodologies. New cleaning solution formulations must effectively clean the residues but should not promote interaction of water with the low-k material, leading to film degradation and increase of k-value. Water interaction between the formulations and porous low-k materials will be investigated using dielectric spectroscopy.

Subtask 2. Surface Preparation of Ge and Si-Ge Films: Cleaning of Ge and Si-Ge structures by aqueous solutions is much more challenging than cleaning Si. Traditional cleaning chemistries used in silicon processing are oxidizing in nature (such as SC-1). Preliminary research shows that because of the solubility of GeO_2 in water Ge surfaces have high etch rates and surface roughening in traditional chemicals such as H_2O_2. Unlike SiO_2, which is sparingly soluble in water, GeO_2 is highly soluble in water. Consequently, a germanium oxide layer is not a suitable passive layer during aqueous processing of Ge. Traditional silicon cleaning also relies on very small amount of etching of the surface oxide film to remove particles. Therefore, much of the cleaning processes developed for Si surfaces cannot be directly applied to these new surfaces. In the processing of Si-Ge alloys, the solubility of GeO_2 can be taken advantage of in etching by hydrogen peroxide. Etching with hydrogen peroxide solutions is highly selective; only at Ge atomic fractions less than 0.7 in Si-Ge alloys can be etched.

One potential approach in the cleaning of Ge based structures is to use non-aqueous formulations containing small amounts of water. One example is the use of organic acids such as acetic acid. Organic acids etch Ge but the extent of etching can be controlled by water content. Another interesting approach is to use reducing chemistries. It is known that cathodic polarization (application of negative potential) can prevent the dissolution of Ge by inhibiting the formation of GeO_2. The solubility diagram in Figure 1 indicates that it is possible to inhibit dissolution of Ge by the application of negative potential and the pH range of reduced solubility is a function of applied potential. Reducing chemicals such as aqueous hydroxylamine can remove particulates through redox reactions. For example, removal of TiO_2 from ashed etch residues can be achieved using hydroxylamine solutions which can reduce tetravalent Ti to trivalent Ti.

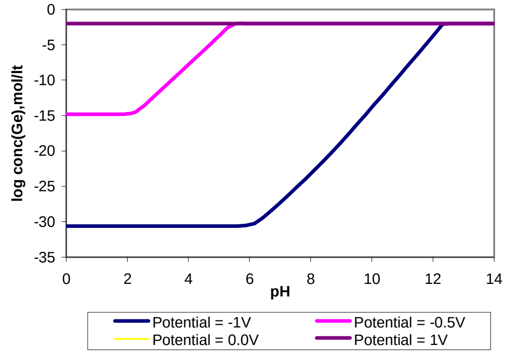

***Figure 1**. Solubility of Ge in water (Ge_T = 0.01 M); solution concentration of 0.01 M implies 100%*

Metallic contamination on semiconductor surfaces can be removed in aqueous solutions with high oxidation potential species. A more fundamental understanding of the new surfaces in aqueous solutions including oxidative H_2O_2 and O_3 is needed to develop an effective and environmentally-friendly cleaning solution. Substrate etch and surface roughening need to be kept at a minimum while achieving optimal metal removal (preliminary results are shown in Figure 2, below). In tandem, a robust metal contamination evaluation method on Ge surfaces needs to be developed. This will involve modifications to VPD ICP-MS and TXRF methods developed for Si surfaces. Ge surface roughening and metal removal efficiencies of diluted H_2O_2 and ozonated de-ionized water solutions will be studied in depth to develop a successful cleaning solution.

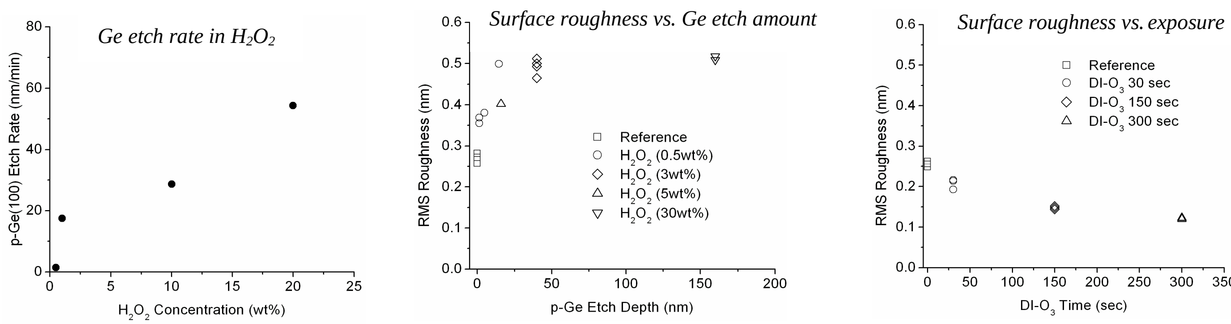

***Figure 2**. Ge etch and roughness in peroxide and DI-ozone cleaning solutions*

<u>*Subtask 3. Cleaning Model*</u>*:* A comprehensive model will be developed to simulate the general cleaning of micro/nano structures by a cleaning liquid. This model will include and integrate the following process steps:

1. Transport of the cleaning liquid from bulk to the surface of the wafer (fluid mechanic considerations)
2. Transport of cleaning fluid into the micro/nano structures
3. Surface interactions which include wetting, chemical interaction with the residue contaminants, and desorption of cleaning reaction by-products

4. Transport of the cleaning by-products out of the micro/nano structures
5. Transport of the cleaning by-products into the bulk of the cleaning fluid

Conclusions:

Ozonated DI water shows approximately 1/10 the etch rate of H_2O_2 and improved surface roughness; moreover, it has significant environmental advantages. Therefore, successful integration and application of these relatively friendly cleaning solutions would represent a win/win situation for both process gain, cost reduction, and environmental gain in a strategic and critical future application.

A process model is developed that will generally apply to both porous low-k as well as pattered wafers with well-defined micro/nano-structures. Step 3 in this sequence will have parameters that depend on the type of material used (Si-based, Ge-based, etc). This model allows analysis of data obtained in subtasks 1 and 2 in a systematic way for determining the fundamental process parameters. These parameters can then be used to compare various processes recipes, cleaning fluids, and operating conditions. The model will be useful for futures field applications as well, where cleaning recipes and procedures need to be fine-tuned for specific applications.